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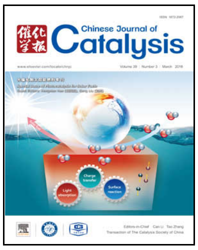

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Photocatalytic water oxidation over $BiVO_4$ with interface energetics engineered by Co and Ni-metallated dicyanamides

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Photocatalytic water oxidation based on semiconductors usually suffers from poor charge transfer from the bulk to the interface, which is necessary for oxygen generation. Here, we construct a hybrid artificial photosynthesis system for photocatalytic water oxidation. The system consists of $BiVO_4$ as the light harvester, a transitional metal complex ($M(dca)_2$, M = Co, Ni, dca: dicyanamide) as the water oxidation catalyst, and $S_2O_8^{2-}$ as a sacrificial electron acceptor. The system exhibits enhanced oxygen evolution activity when $M(dca)_2$ is introduced. The $BiVO_4/Co(dca)_2$ and $BiVO_4/Ni(dca)_2$ systems exhibit excellent oxygen evolution rates of 508.1 and 297.7 μmol/(h·g) compared to the pure $BiVO_4$ which shows a photocatalytic oxygen evolution rate of 252.2 μmol/(h·g) during 6 h of photocatalytic reaction. $Co(dca)_2$ is found to be more effective than $Ni(dca)_2$ as a water oxidation catalyst. The enhanced photocatalytic performance is ascribed to the $M(dca)_2$-engineered $BiVO_4$/electrolyte interface energetics, and to the $M(dca)_2$-catalyzed surface water oxidation. These two factors lead to a decrease in the energy barrier for hole transfer from the bulk to the surface of $BiVO_4$, which promotes the water oxidation kinetics.

1. Introduction

Developing techniques for producing renewable and clean fuels is necessary to deal with increasing energy and environmental issues [1,2]. Photocatalytic water splitting is one of the most attractive methods for utilizing solar energy for H_2 production [3,4]. However, the four-electron oxygen evolution reaction (OER) is generally considered to be the bottleneck for the water splitting reaction owing to its sluggish kinetics, multiple-electron transfer, and complicated O–O bond formation [5]. Numerous efforts have therefore been devoted to developing efficient water oxidation catalysts (WOCs) in the past few decades [6,7], since the pioneering work of Gersten et al. [8].

Metal oxide semiconductors have been widely studied for photocatalytic water splitting, because of their suitable band structures and high stability [9]. $BiVO_4$ with a bandgap of 2.4 eV has received much attention. However, $BiVO_4$ suffers from excessive charge recombination, low charge transport efficiency, and slow water oxidation kinetics. Strategies such as morphology control, hybridizing with other materials, and doping have been attempted to improve the photocatalytic performance of $BiVO_4$ [10]. WOCs can also effectively reduce the recombination rate of photoinduced charge carries, which in turn improves the photocatalytic water oxidation. Noble metal-based WOCs such as $Ru(bpy)_3^{2+}$ and IrO_2 have been widely employed for this purpose, and exhibit very high activities for water oxidation. However, their high cost and scarcity limit their scalable application. Catalysts consisting of more abundant elements

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such as Co, Ni, Fe, Mn, and Bi are more promising in this respect. In particular, transitional metal-based molecular complexes have attracted increasing attention in the past few years, because of their low cost, tailorable structures, and homogeneous properties. A promising approach is combining molecular WOCs with semiconductors to utilize the advantages of both molecular complexes and metal oxides for efficient photocatalytic oxygen evolution. Niu *et al.* [11] reported a system consisting of semiconductor quantum dots and an acetaminosalol cobalt(II) complex, which exhibited considerable activity and good stability during 72 h of photocatalytic reaction.

In the current study, we report a hybrid system consisting of $M(dca)_2$ (where M is a metal; dca is dicyanamide) as a WOC and $BiVO_4$ as the photosensitizer, for photocatalytic oxygen evolution in aqueous solution. Both $BiVO_4/Co(dca)_2$ and $BiVO_4/Ni(dca)_2$ exhibit better performance than pure $BiVO_4$, with turnover numbers (TONs) of 3.46 and 2.03 after 6 h of photocatalytic reaction, respectively. $BiVO_4/Co(dca)_2$ also possesses considerable photocatalytic activity after 30 h under visible light irradiation. Surface photovoltage (SPV) and electrochemical measurements show that efficient hole transfer from $BiVO_4$ to $M(dca)_2$ results in high charge separation efficiency, which in turn promotes the water oxidation reaction kinetics. It is demonstrated that the water nucleophilic attack (WNA) pathway could be responsible for the photocatalytic water oxidation. These findings provide insights for constructing earth-abundant element-based photocatalytic systems for efficient and stable oxygen evolution in aqueous solution.

2. Experimental

2.1. Materials

$Co(NO_3)_2·6H_2O$, $Ni(NO_3)_2·6H_2O$, $NaN(CN)_2$, $Bi(NO_3)_3·5H_2O$, NH_4VO_3, $Na_2S_2O_8$, Na_2SO_3, urea, ethanol, and *N*,*N*′-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Fluorine-doped tin oxide (FTO) coated glass was purchased from Nippon Sheet Glass Co., Ltd, Japan. All materials were of analytical grade and used without further processing. Millipore deionized water (resistivity: 18.25 MΩ·cm) was used throughout all experiments.

2.2. Syntheses of samples

2.2.1. Synthesis of $BiVO_4$

$BiVO_4$ was prepared by a simple homogeneous precipitation method according to the literature [5]. Typically, 19.4 g of $Bi(NO_3)_3·5H_2O$ was added into 100 mL of water and stirred for 20 min to form a homogeneous solution. Simultaneously, 4.68 g of NH_4VO_3 was dissolved into 100 mL of water to form another solution. The two solutions were mixed, followed by the addition of 7.5 g of urea and then heating to 90 °C under stirring. After the crystallization of $BiVO_4$, the obtained slurry was stirred at 90 °C for 24 h to form the precipitate, which was then washed with water, collected by filtration, and dried at 45 °C.

2.2.2. Synthesis of $M(dca)_2$ (M = Co, Ni)

$M(dca)_2$ was synthesized according to a method reported previously [12]. In a typical synthesis, 5 mmol of $Co(NO_3)_2·6H_2O$ or $Ni(NO_3)_2·6H_2O$ was dissolved in 20 mL of water; 10 mmol of $NaN(CN)_2$ was added into 20 mL of DMF. Then, the $NaN(CN)_2$ solution was slowly added into the $Co(NO_3)_2$ or $Ni(NO_3)_2$ aqueous solution. The resulting suspension was stirred at room temperature for 12 h. Finally, the resulting precipitate was collected by filtration, washed with ethanol, and dried at 60 °C in a vacuum oven.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of samples were collected using an X'Pert PRO MPD X-ray diffractometer (PANalytical, Netherlands) with (u/2u) Bragg-Brentano geometry (Ni filter; Cu K_α radiation; λ = 0.1541874 nm). UV-Vis absorption spectra of $M(dca)_2$ solutions were collected using a Cary 7000 UV-Vis-near-IR spectrophotometer with a blank solution as the reference. Fourier-transform infrared (FT-IR) spectra were collected using a Nicolet Magna 670 FT-IR spectrometer. SPV spectra were collected using a PL-SPS1000 spectrometer (Beijing Perfectlight Technology Co., Ltd., P. R. China) with a monochromatic light source [13] and an irradiation range from 400 to 600 nm. The amount of molecular catalyst present during the photocatalytic O_2 evolution process was determined using inductively-coupled plasma mass spectrometry (ICP-MS, ICPE-9000*, Shimadzu, Japan). Typically, 0.5 mL aliquots of the photocatalytic system suspension were removed at intervals using syringe pumps, followed by high-speed centrifugation (15000 r/min for 10 min) to obtain supernatants for ICP-MS tests. X-ray photoelectron spectrometry (XPS) (AXIS Ultra DLD, Shimadzu/Kratos Analytical, Japan) was used to detect the surface chemical components and states of samples, with monochromatic Al K_α radiation (150 W, 15 kV, 1486.6 eV) under high vacuum ($< 3.9 \times 10^{-10}$ kPa).

2.4. Photocatalytic tests

Photocatalytic oxygen production experiments were carried out in a 100 mL Pyrex glass cell under visible light. The light source was a 300 W Xe arc lamp (PLSSXE300, Beijing Trusttech Technology Co., Ltd, P. R. China) equipped with a 420 nm cut-off filter. In a typical photocatalysis experiment, 15 mg of $BiVO_4$ powder as a photosensitizer was well dispersed in an aqueous solution (70 mL) containing 5 mg of $M(dca)_2$ as a WOC and 0.8 g of $Na_2S_2O_8$ as a sacrificial electron acceptor. The reaction solution was purged with Ar for 30 min to remove air before irradiation. The evolved gas was detected by gas chromatography (GC, SP-2100, Beijing Beifen-Ruili Analytical Instrument Co., Ltd, P. R. China) equipped with a thermal conductivity detector (TCD) and TDX-01 column. Argon was used as the carrier gas. No oxygen production was detected in the control experiment in the absence of irradiation.

2.5. Adsorption measurement

The amount of $M(dca)_2$ adsorbed on $BiVO_4$ was calculated